

THERMAL AND ELECTRICAL CONDUCTIVITY PROPERTIES OF SOME Cr^{III}, Mn^{II} AND UO₂^{II} AMINO ALCOHOL COMPLEXES

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Abstract

Cr^{III}, Mn^{II} and UO₂^{II} amino alcohol complexes were prepared and analyzed. The IR spectra proved that the ligation occurs via oxygen and nitrogen atoms. The nujol mull electronic absorption spectra joined with the room temperature magnetic moment values proved that the complexes are of O_h geometry. The thermal behaviour of the complexes was studied by DTA and TG techniques. The mechanism of the decomposition was suggested. The thermodynamic parameters of the decomposition were evaluated and discussed. The entropy of activation changes, ΔS^{\ddagger} , showed that the transition states are more ordered than the reacting complexes. The D.C. electrical conductivity measurements of Cr- and Mn-amino alcohol complexes are of semiconductor behaviour. Empirical equations were deduced for the conduction of the investigated complexes.

Keywords: amino alcohol complexes, electrical conductivity, thermal analysis

Introduction

Amino alcohol complexes received much interest because of their application in different fields [1–4]. In our laboratory, extensive studies on the structural chemistry of the amino alcohol complexes were reported [5–16]. The transition metal complexes were of different stereochemistries. Equilibrium studies were reported for some transition metal amino alcohol complexes, based on potentiometric, spectroscopic and polarographic measurements. In a sequel continuation, the present work is aimed to study some thermal and electrical properties of the entitled complexes, not reported before.

Methods of calculations

The reaction order of the thermal reactions is calculated using Kissinger approach [17], depending on the application of different heating rates. The values of collision factor, Z , can be obtained in case of Horowitz Metzger by making the use of the relation [18]:

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$$Z = \frac{\Delta E_a}{RT_m} \beta \exp\left(\frac{\Delta E_a}{RT_m}\right)$$

Also, the entropies of activation (ΔS^*) can be obtained from the relation [19]:

$$Z = \frac{KT_m}{h} \exp\left(\frac{\Delta S^*}{R}\right)$$

where R represents molar gas constant, β is the rate of heating (K s^{-1}), K is Boltzmann constant and h is the Planck's constant.

The activation energy, ΔE_a , of the thermal decomposition step is determined from the slope of the straight line of the $\ln \Delta T$, $1/T$ relationship. The slope is of Arrhenius type and equals to $-\Delta E_a/R$.

The dependence of the electrical conductivity on temperature is expressed by the following equation: $\sigma = \sigma^0 \exp -\Delta E/KT$, where ΔE is the activation energy for the conduction, σ^0 is a constant for the conductivity independent of temperature and K is the Boltzmann constant.

Experimental

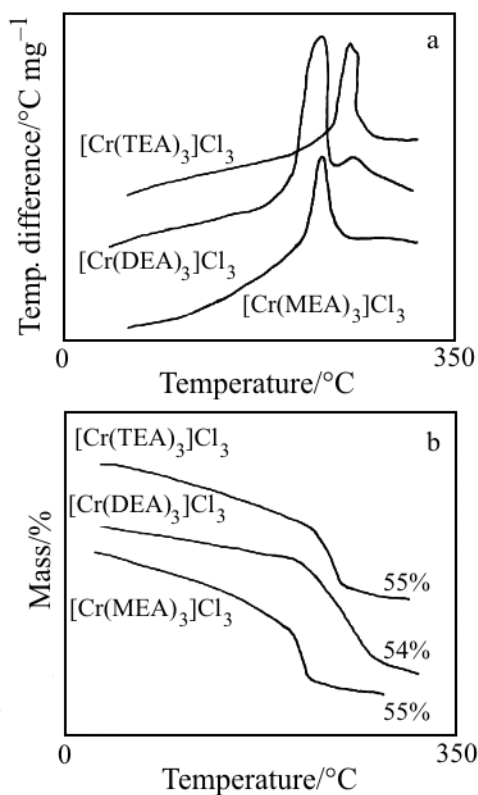
The solid metal-ethanolamine complexes were prepared by mixing 0.1 mol of the metal salts, CrCl_3 , MnCl_2 and $\text{UO}_2(\text{CH}_3\text{COO})_2$, dissolved in 15 mL distilled water with the calculated amount of the ligand saturated in ethanol to attain the ratios 1:1, 1:2 and 1:3 metal to ligand. The mixture was refluxed for about 5 min. The complexes were precipitated and filtered, then washed several times with a binary mixture of $\text{EtOH-H}_2\text{O}$ then dried in a desiccator over anhydrous CaCl_2 . The chromium and manganese contents were determined by the usual complexometric titration procedures [20]. Uranium analysis was performed gravimetrically by igniting the complexes in a muffle furnace at 800°C and weighing as U_3O_8 . The halogen content was determined by burning 30 mg of the sample in an oxygen flask in the presence of $\text{KOH-H}_2\text{O}_2$ mixture and titrating with a standard $\text{Hg}(\text{NO}_3)_2$ solution using diphenyl carbazone indicator [21]. The analytical data, colour and mp. of the prepared complexes are collected in Table 1. Ultraviolet and visible spectra were recorded using Perkin Elmer spectrophotometer model Lambda 4B covering the wavelength range 190–900 nm. The complexes were measured in nujol mull, following the method described by Lee *et al.* [22]. The KBr disk IR spectra were recorded using Perkin Elmer spectrophotometer model 1430 covering the frequency range $200\text{--}4000\text{ cm}^{-1}$. The room temperature molar magnetic susceptibilities, corrected for diamagnetic using Pascal's constants, were determined using Faraday's method [23].

Thermogravimetric and differential thermal analysis were performed on a DuPont 9900 computerized thermal analyzer in the temperature range $25\text{--}350^\circ\text{C}$. The heating rate was $10^\circ\text{C min}^{-1}$. 60 mg of the sample was placed in a platinum crucible. Dry nitrogen was flowed over the sample at a rate $10\text{ cm}^3\text{ min}^{-1}$ and a chamber cooling water flow rate was $10\text{ L}^{-1}\text{ h}^{-1}$. Fig. 1 shows an example of the thermograms.

The electrical measurements were measured in the temperature range $289\text{--}423\text{ K}$. The complexes were prepared in the form of tablets at a pressure of 4 ton cm^{-2} . The tab-

Table 1 Analytical data, colour and *m.p.* (°C) of metal amino alcohol complexes

Complex	Colour	<i>M.p.</i> /°C	%Found (%Expected)	
			M	Cl
[Cr(HL ¹) ₃]Cl ₃	grey green	235.0	15.01 (15.22)	31.16 (31.17)
[Cr(H ₂ L ²) ₃]Cl ₃	grey green	236.3	10.89 (10.98)	22.39 (22.49)
[Cr(H ₃ L ³) ₃]Cl ₃	grey green	239.8	8.48 (8.59)	17.43 (17.59)
[Mn(HL ¹) ₃]Cl ₂	brown	210.0	17.69 (17.77)	22.89 (22.96)
[Mn(H ₂ L ²) ₃]Cl ₂	brown	200.0	12.38 (12.46)	16.06 (16.10)
[Mn(H ₃ L ³) ₃]Cl ₂	brown	203.0	9.47 (9.59)	12.32 (12.39)
[UO ₂ (HL ¹) ₂]Ac ₂	orange	245.0	46.49 (46.66)	–
[UO ₂ (H ₂ L ²) ₂]Ac ₂	yellow	343.0	39.63 (39.80)	–
[UO ₂ (H ₃ L ³) ₂]Ac ₂	yellow	330.0	34.58 (34.70)	–

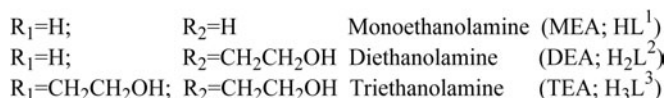
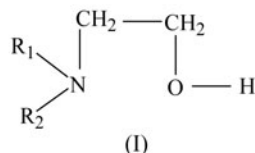
HL¹=MEA, H₂L²=DEA, H₃L³=TEA**Fig. 1** a – DTA and b – TG patterns of Cr^{III}-amino alcohol complexes

lets were of an area 2.54 cm^2 and thickness 0.12 cm . The samples were held between two copper electrodes with a silver paste inbetween and inserted with the holder vertically into cylindrical electric furnace. The potential drop across the heater was varied gradually through variac transformer to produce slow rate of increasing temperature to get accurate temperature measurements. The circuit used to measure the electric conductivity consists of D.C. regulated power supply Heat Kit (0–400 V), Keith multimeter for measuring current with a sensitivity up to 10^{-15} A . The temperature of the sample was measured within $\pm 0.1^\circ\text{C}$ by means of copper-constantane thermocouple. The conductivity was obtained in the case of cooling using the general formula: $\sigma = Id/V_c a$, where I is the current in ampere, V_c is the potential drop across the sample of cross section area ' a ' and thickness ' d '.

Results and discussions

Structural chemistry of the amino alcohol complexes

It was reported that the IR spectra of the amino alcohol ligands(I), gave characteristic bands due to ν_{OH} , ν_{NH_2} , ν_{CH_2} , δ_{OH} , δ_{CH_2} , ν_{CN} , τ_{CH_2} , $\nu_{\text{C-C}}$, γ_{OH} are assigned. The low intensity of the wagging vibration band of NH_2 group supports the existence of an internal hydrogen bond in MEA ligand [24] and the broadness of all vibrations of the $-\text{OH}$ groups is mainly due to strong intermolecular hydrogen bonds in the three ligands.

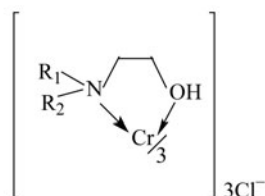


However, mono-, di- and triethanolamine compounds gave 1:3 Cr^{III} and Mn^{II} complexes, while UO_2^{II} gave the 1:2 complex.

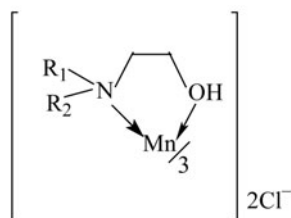
The IR spectra of the complexes indicated that the coordination occurs through both nitrogen and oxygen sites, as recorded from the shifts of OH and NH_2 (or NH) bands beside the appearance of $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$ bands. In case of UO_2^{II} complexes additional IR bands corresponding to the UO_2 vibrations are observed at $925\text{--}930$, $810\text{--}860$ and $245\text{--}270 \text{ cm}^{-1}$. The nujol mull electronic absorption spectra joined with the room temperature magnetic moment values of the complexes gave the following:

1) Each Cr^{III} complex is with two bands due to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}(\text{F})$ transitions at 573 and 403 nm for MEA complex ($\mu_{\text{eff}} = 4.30 \text{ BM}$), at 569 and 403 nm for DEA complex ($\mu_{\text{eff}} = 5.07 \text{ BM}$) and at 570 and 402 nm for the TEA complex ($\mu_{\text{eff}} = 5.40 \text{ BM}$). This indicates the O_h geometry of the Cr^{III} complexes with high spin nature [25]:

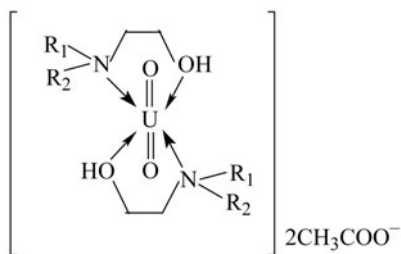
2) Each Mn^{II} complex gave one weak broad band at about 340–370 nm indicating the O_h geometry of the complexes [25]. The weak O_h field of Mn^{II} has one electron in each

[Cr(EA)₃]Cl₃, EA=MEA, DEA or TEA

d-orbital and their spins are parallel, making it sextuplet spin. This corresponds to ⁶S ground state of the Mn^{II} ion which is not splitted by the ligand field. This is the only sextuplet state possible for every conceivable alternation of the electron distribution $t_{2g}^3 e_g^2$, with all spins parallel, resulting in the pairing of the two or four spins thus making quarted or doublet states. Hence all excited states of *d*⁵ system have different spin multiplicity from the ground state and the transitions to them are spin forbidden. Because of weak spin orbit interactions, such transitions are not totally absent but they may give a very weak broad band like that observed. The μ_{eff} values are 5.99, 6.17 and 6.30 BM for Mn complexes derived from MEA, DEA and TEA, respectively, indicating the sextuplet state of the Mn^{II} ion in these complexes [25]:

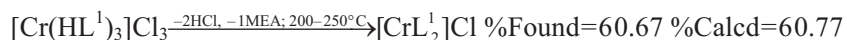
Mn(EA)₃]Cl₂, EA=MEA, DEA or TEA

3) Each UO₂^{II} complex showed three bands. The absence of any band over 500 nm proved that the complexes have more than four equatorial groups [26, 27]. The band around 350 nm assigned the excited state of the uranyl ion [28]. The band at ~430 nm was attributed to ¹E_g⁺ → ³Π_u transition. All uranyl complexes were diamagnetic and of O_h geometry. The acetate ions were in the outersphere. This fact is proved by the solubility of the complexes in water and determination of the acetate ions as silver acetate gravimetrically.

[UO₂(EA)₂](CH₃COO)₂, EA=MEA, DEA or TEA

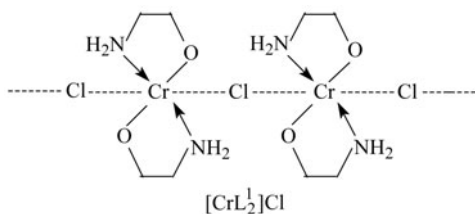
Thermal analysis of the amino alcohol complexes

The DTA pattern of $[\text{Cr}(\text{HL}^1)_3]\text{Cl}_3$ complex gave one exothermic peak at 235°C with an activation energy of $229.5 \text{ kJ mol}^{-1}$ and an order of 0.98. Its TG is due to removal of 2HCl molecules and 1MEA molecule, Fig. 1 gives a representative example of a) DTA and b) TG patterns of Cr^{III} - amino alcohol complexes.

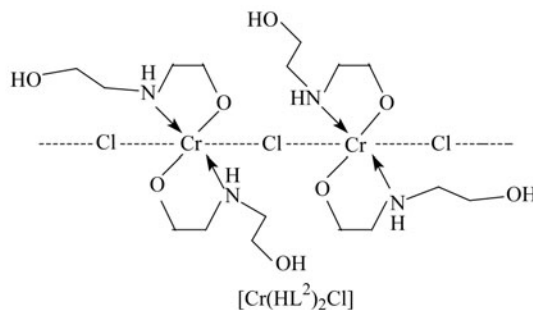


The IR spectra of the resulting species proved the deprotonation of the hydroxyl group of the ligand accompanied with the disappearance of ν_{OH} .

The UV-Vis. spectra gave two bands at 570 and 410 nm of the O_h structure of the species. These data gathered with the insolubility of the formed species drive us to the following structure:



The DTA pattern of $[\text{Cr}(\text{H}_2\text{L}^2)_3]\text{Cl}_3$ complex gave two exothermic peaks at 226 and 252°C with activation energies of 247.42 and $150.28 \text{ kJ mol}^{-1}$ and orders of 0.828 and 1.26, respectively. Its TG proceeds in a similar manner to that of the MEA in the 1st step followed by another step where two moles of H_2O liberated in the 2nd step. The decomposition pattern can be given as follows:



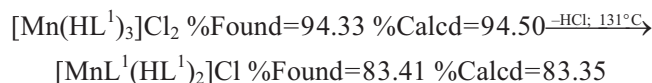
Also the $[\text{Cr}(\text{HL}^2)_2 \text{Cl}]$ species were found, by IR and UV-Vis. spectra, to be bridged chloro complex with O_h geometry as follows:

The last species were also of bridged chloro complex to lose $2\text{H}_2\text{O}$ molecules from the DEA ligands.

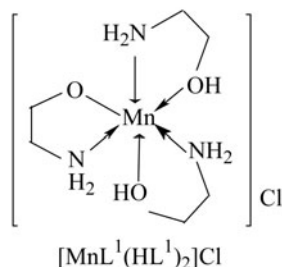
The $[\text{Cr}(\text{H}_3\text{L}^3)_3]\text{Cl}_3$ complex showed one exothermic DTA peak at 240°C with an activation energy of $196.73 \text{ kJ mol}^{-1}$ and an order of 0.96. The TG of the residual species of the decomposition was like that of the DEA complex, where 2HCl and 1TEA molecules are liberated, with the decomposition of the TEA ligand itself. The decomposition pattern may be assumed like that of DEA complex, proceeds in two steps while that of the TEA complex is in one step.

The exothermic peaks of chromium complexes are probably due to the result of bond breaking and bond formation mechanisms. Such view lets to assume the impacting of the polymer species formed in the decomposition steps, consequently the energy liberated in the polymer formation is higher than that consumed in bond breaking.

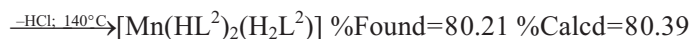
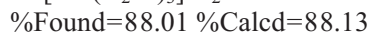
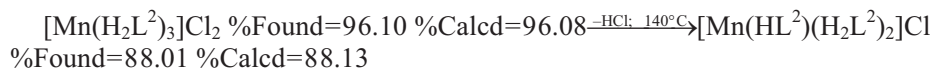
The DTA pattern of $[\text{Mn}(\text{HL}^1)_3]\text{Cl}_2$ complex gave two endothermic peaks at 78 and 131°C with activation energies of 73.81 and $182.79 \text{ kJ mol}^{-1}$ and orders of 1.26 and 1.20, respectively. The TG of this complex indicates that the 1st peak was due to the loss of adsorbed water molecule. The 2nd peak was due to the removal of one HCl molecule. The scheme of the degradation of this complex is assumed to be as follows:



The species $[\text{MnL}^1(\text{HL}^1)_2]\text{Cl}$ was subjected to solubility in polar solvents, like H_2O , and it was found that this species are greatly soluble in the polar solvents. This indicated that chloride ion is in the outersphere. The UV-Vis. spectra of this fragment showed same spectral peak of the origin complex indicating the same O_h geometry.



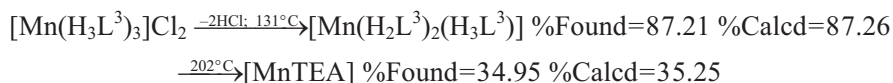
The DTA pattern of $[\text{Mn}(\text{H}_2\text{L}^2)_3]\text{Cl}_2$ complex gave three endothermic peaks. The 1st at 85.26°C assigned the loss of adsorbed water molecule. The 2nd and the 3rd peaks with activation energies of 263.9 and $289.0 \text{ kJ mol}^{-1}$ and orders of 1.63 and 1.26, respectively, are found to be, by TG, due to removal of 2HCl molecules separately as follows:



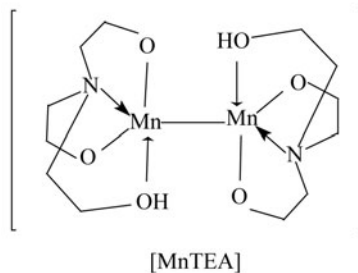
The spectra of both $[\text{Mn}(\text{HL}^2)(\text{H}_2\text{L}^2)_2]\text{Cl}$ and $[\text{Mn}(\text{HL}^2)_2(\text{H}_2\text{L}^2)]$ complexes and the solubility of the former complex, which indicates the chloride ion is in the outersphere, proved that both are of O_h geometry.

The DTA pattern of $[\text{Mn}(\text{H}_3\text{L}^3)_3]\text{Cl}_2$ complex gave two endothermic peaks at 131 and 202°C with activation energies of 104.40 and 251.99 kJ mol^{-1} and orders of 1.75 and 1.26, respectively. The TG of this complex indicates that the 1st peak was due to the removal of 2HCl molecules. The 2nd peak was due to the beginning decomposition of the TEA ligands leading later to $[\text{MnTEA}]$ species.

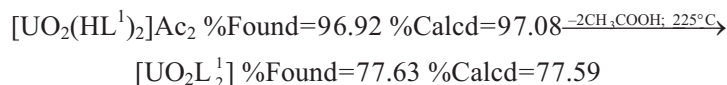
The UV-Vis of $[\text{MnTEA}]$ species showed 5-coordinated geometry as follows:



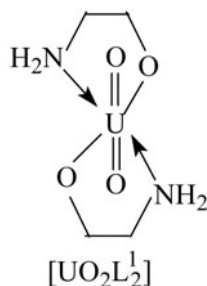
The structure of the $[\text{MnTEA}]$ complex is assumed to have Mn–Mn bond to satisfy the stability of the 5-coordinate geometry as follows:



The $[\text{UO}_2(\text{HL}^1)_2]\text{Ac}_2$, $\text{Ac}=\text{CH}_3\text{COO}$, complex gave two DTA peaks at 89.74 and 255°C. The 1st peak was due to the removal of one water molecule. The 2nd peak with activation energy of 101.65 kJ mol^{-1} and order of 0.92, assigned, by TG, the removal of 2 CH_3COOH molecules. The decomposition steps may be summarized as follows:

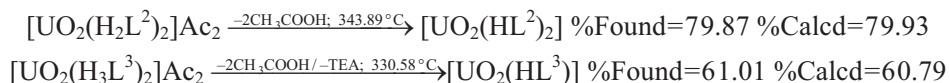


The UV-Vis. spectra of $[\text{UO}_2\text{L}_2^1]$ proved the O_h geometry since no peaks appeared over 500 nm indicating the more 4 equatorial groups [28].



Both $[\text{UO}_2(\text{H}_2\text{L}^2)_2]\text{Ac}_2$ and $[\text{UO}_2(\text{H}_3\text{L}^3)_2]\text{Ac}_2$ complexes gave one DTA peak for each at 343.59 and 330.58°C, with orders of 0.95 and 0.98, respectively.

The TG proved that the peak of the DEA complex was due to removal of 2CH₃COOH molecules, similar to the 2nd step of MEA complex, and the peak of the TEA complex was due to removal of the 2CH₃COOH molecules with the degradation of the TEA molecules. The decomposition pattern of these two complexes may be summarized as follows:



The residual species were found to have O_h geometry, by UV spectra, since no bands appeared above 500 nm.

The change of the entropy of activation ΔS^* in the range of -0.098 to -1.194 kJ mol⁻¹ for the thermal decomposition steps, showed that the transition states are more ordered, i.e. in a less random molecular configuration, than reacting complexes. The fractions appeared in the calculated orders of the thermal reactions confirmed that the reactions proceeded in somewhat complex mechanisms.

In conclusion, the thermal pattern of the decomposition steps of the investigated complexes showed that M-ligand bonds dissociated after removal of small molecules, HCl in case of Cr^{III}, Mn^{II} complexes and CH₃COOH in the UO₂^{II} complexes. This reflects the stability of the rings between the amino alcohol ligands and the central metal ion.

Comparing the thermal behaviour of Cr^{III} and Mn^{II} complexes, showed that due to the higher charge of Cr^{III} than Mn^{II}, Cr^{III} tends to form bridged chloro complexes keeping the O_h geometry, Mn^{II} does not.

Electrical conductivity of the amino alcohol complexes

The electrical conductivity data are collected in Table 2. The data depict that all complexes are of semiconductor behaviour. The discontinuation in the conductivity curves of the complexes can be argued to be a molecular rearrangement or crystallographic transition, due to traps formation or delocalization, due to semiconductor behaviour.

Plotting $\ln \sigma$ vs. $1000/T$ of the Cr-MEA and Cr-TEA complexes illustrated that both complexes exhibit semiconducting properties. The conductivity at low temperature regions has negative temperature coefficient while, that at high temperature, >87°C, the conductivity increases with temperature. The breaks at 71.8 and 86.7°C for Cr-MEA and Cr-TEA complexes, respectively, are due to the loss of the adsorbed water molecules.

The activation energies for the conduction are collected in Table 2. The $\Delta E - \ln \sigma_0$ curve gave the following equation for the conduction of chromium complexes:

$$\Delta E = 0.0375 \ln \sigma_0 + 0.7193$$

Table 2 Electrical conductivity properties of some amino alcohol complexes

Complex	$\Delta E/eV$	$\ln\sigma_0$	Transition temperature/ $^{\circ}C$
[Cr(HL ¹) ₃]Cl ₃	0.681 -0.052	-3.0 -22.0	71.8
[Cr(H ₃ L ³) ₃]Cl ₃	0.250 -0.138	-9.5 -22.0	86.7
[Mn(HL ¹) ₃]Cl ₂	-0.121 -0.767	-17.9 -32.5	49.6
[Mn(H ₃ L ³) ₃]Cl ₂	-0.075 -1.428	-52.5 -16.5	68.3

HL¹=MEA, H₂L²=DEA, H₃L³=TEA

The temperature dependence of the conductivity curves of the manganese complexes, showed that at low temperature, <49.6 $^{\circ}C$ is of higher conductivity than that of high temperature.

The conductivity pattern of the Mn-MEA and Mn-TEA complexes exhibit transition temperatures of 49.6 and 68.3 $^{\circ}C$, respectively. The breaks are due to the loss of water molecules exist in the outer sphere of the complexes.

The $\Delta E - \ln\sigma_0$ curve gave the following empirical equation for the conduction of manganese complexes:

$$\Delta E = -0.0201 \ln\sigma_0 + 1.1958$$

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